TECHNICAL REPORT

A Measurement of the Diffusion Coefficient and Radiative Lifetime of Nitrogen Molecules in the $A^3\Sigma_u^+$ State

Technical Report No. 1

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(NASA CR 52469)

4754008

Aug. 1963 7p refs
Submitted for Publication

[6]

NASA Research Grant NsG193-63

Prepared for

National Aeronautics and Space Administration

Washington, D. C.

[redacted]

FORWARD

This report, by E. C. Zipf, Jr., consists of a manuscript which has been published in the Journal of Chemical Physics, 38, 2034 (1963).

The work reported herein is part of this laboratory's upper atmosphere program in which rocket spectrometric experiments are correlated with laboratory observations in the analysis of atomic and molecular processes occuring in the region above 80 kilometers.

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A Measurement of the Diffusion Coefficient and Radiative Lifetime of Nitrogen Molecules in the $A^3\Sigma_u^+$ State

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We have obtained a value for the diffusion coefficient and radiative lifetime of nitrogen molecules in the metastable $A^3\Sigma_u^+$ ($v' = 0$) state by measuring the intensity of the (0, 6) Vegard-Kaplan band ($A^3\Sigma_u^+ \longrightarrow X^1\Sigma_g^+$) as a function of time and pressure in the afterglow of a microwave discharge in very pure nitrogen.

The discharge took place in a small cylindrical quartz cell located at the center of a microwave cavity resonant in the TM_{010} mode at 2900 Mc/sec. The gas was excited periodically by microwave power pulses from a QK-60 magnetron. The afterglow was characterized by comparatively strong emission of the Vegard-Kaplan bands and the second positive system of nitrogen, but by only weak emission of the first positive bands. Time sampling techniques[1] were used to measure the intensity of the Vegard-Kaplan bands during the afterglow. Table I lists the more intense bands that were observed.

Table I

Vegard-Kaplan bands observed in the afterglow

v', v''	I	v', v''	I	v', v''	I
0, 3	2	1, 4	2	1, 10	9
0, 4	4	1, 5	2	2, 7	2
0, 5	8	1, 8	7	3, 6	2
0, 6	10	1, 9	10	4, 8	1

In order to minimize the effects of impurities, an Alpert-type ultra-high vacuum system[2] was used in this work. Vacuua of the order of 10^{-9} mm Hg were normally obtained following a bakeout at 410°C for 35 hours. Hydrocarbon contamination was reduced to a minimum by isolating the discharge cell from the diffusion pump with an activated alumina trap.[3] Very pure nitrogen was obtained by passing Airco reagent-grade nitrogen over hot (300°C), oxygen-free copper and then storing the gas over a freshly evaporated nickel film. The nickel film further purified the gas by selectively absorbing O_2, H_2, CO_2, CO, and some hydrocarbons, but not nitrogen, at room temperature.[4] In addition to emitting the Vegard-Kaplan bands, the treated gas differed in several other respects from unprocessed reagent-grade nitrogen: It was more difficult to ionize and it produced a lower degree of ionization for the same power input to the cavity.

Late in the afterglow nitrogen molecules in the $A^3\Sigma_u^+$ state are destroyed by collisions with other gas molecules, by radiation of the Vegard-Kaplan bands, and by fundamental mode diffusion to the walls of the discharge cell. The density of molecules, N, in the $v' = 0$ level of the $A^3\Sigma_u^+$ state will decay exponentially with time

$$N = N_0 J_0 (\beta_1 r/a) \cos (\pi z/h) \exp(-\nu_m t) \qquad (1)$$

where $\beta_1 = 2.405$, a is the radius and h is the height of the discharge cell. If we assume that no appreciable repopulation of the $A^3\Sigma_u^+$ state occurs late in the afterglow, the frequency ν_m is given by

$$\nu_m = \frac{D_m}{\Lambda^2} + \frac{1}{\tau} + \eta \qquad (2)$$

where τ is the radiative lifetime of the $v' = 0$ level, D_m is the metastable diffusion coefficient, η is the frequency of depopulating collisions with other gas molecules and Λ is the fundamental diffusion length of the discharge cell. Values for D_m, η, and τ may be obtained from an analysis of the pressure dependence of ν_m.

Time resolved measurements of the intensity of the (0, 6) Vegard-Kaplan band (figure 1) and of the spatial distribution of N were made in the afterglow. These studies show that the metastable molecules were diffusing in the fundamental diffusion mode late in the afterglow when the intensity of the (0, 6) Vegard-Kaplan band was decaying exponentially with time. Higher mode diffusion and the creation of additional molecules in the $A^3\Sigma_u^+$ state due to the emission of the first positive bands were important processes early in the afterglow. However, the first positive bands were only weakly excited and our data indicate that the repopulation of the $v' = 0$ level by this mechanism was unimportant late in the afterglow.

By measuring ν_m from the data of figure 1 and similar curves in the pressure range 0.1 to 10 mm Hg, we found that $D_m = 0.202$ cm^2 sec^{-1} at 760 mm Hg and 300 ° K, and that τ was about 0.9 sec. No de-excitation of the metastable molecules due to collisions with other gas molecules was observed in pure nitrogen. However, with contaminated gas a two-body quenching process was observed. Further studies on the collisional depopulation of the $A^3\Sigma_u^+$ state are in progress.

The self-diffusion coefficient, D_{11}, of nitrogen has a value[5] of 0.214 cm^2 sec^{-1} at 760 mm Hg and 300° K. Comparison of D_m with D_{11} shows that nitrogen molecules in the excited $A^3\Sigma_u^+$ $(v' = 0)$ state diffuse at a slightly slower rate than ground state molecules. Our value for the radiative lifetime of the $v' = 0$ level is in agreement with the measurements of Noxon.[6]

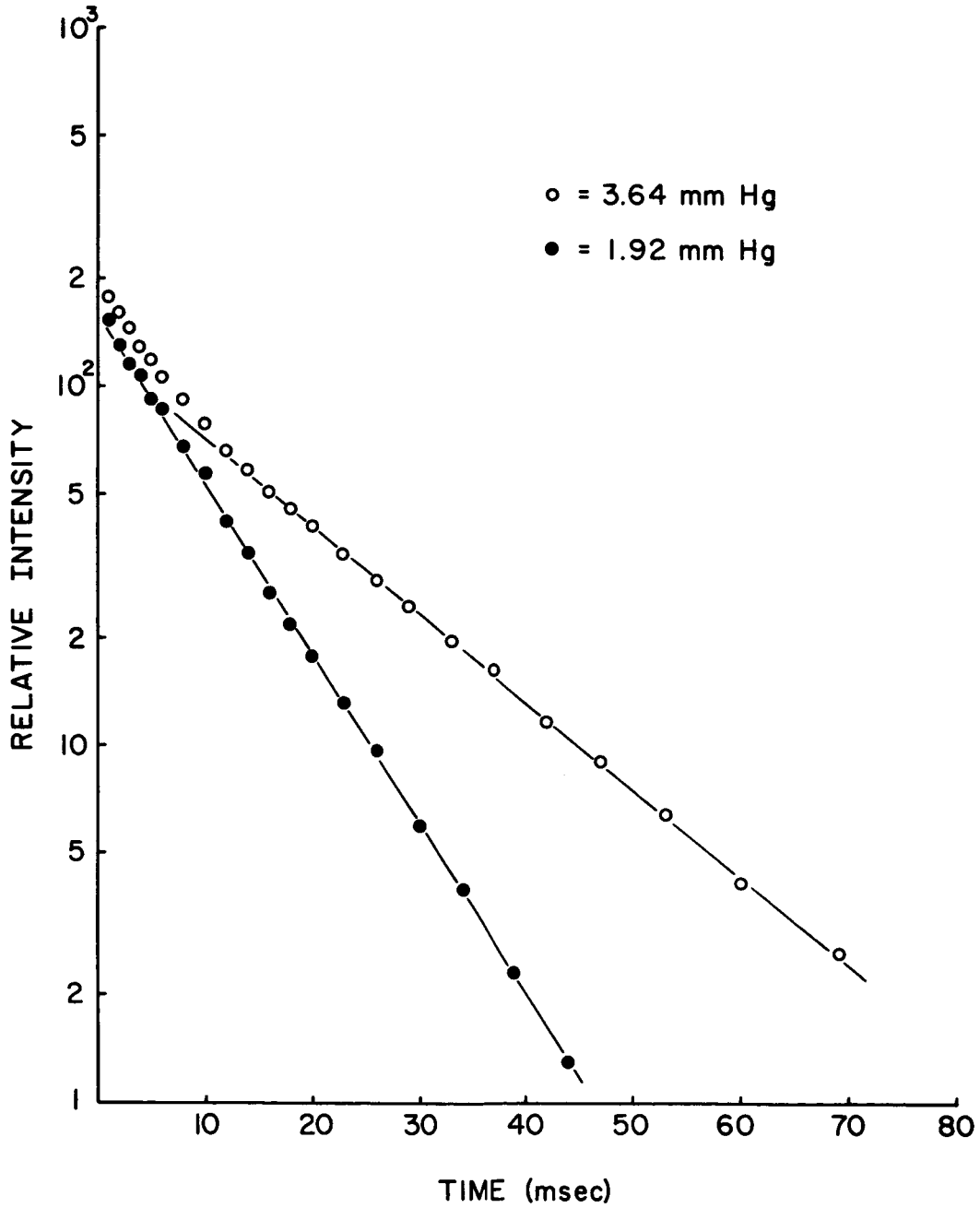

Figure 1. The relative intensity of the (0, 6) Vegard-Kaplan band in the afterglow plotted versus time. $\Lambda^2 = 0.772$ cm^2.

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